Dipolar correlation function and motional narrowing in finite two-dimensional spin systems

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A statistical treatment is used to describe the dipole–dipole relaxation processes of spins $S = 1/2$ diffusing on finite two-dimensional (2*D*) surfaces. This leads to a general expression for the dipolar correlation function $G(\tau)$ including pairwise autocorrelation and cross-correlation terms. We show that for a finite 2*D* planar surface, $G(\tau)$ decays faster than that for an infinite planar surface. For finite 2*D* planar surfaces, dipolar translational correlation times, $\bar{\tau}_c$ are expressed in terms of the diffusion coefficient, the distance of closest approach between spins, and the area of the surface. It is shown that there is rapid motional line shape narrowing for sufficiently small two-dimensional surfaces. The calculation of resonance line shapes for the infinite 2*D* surface is discussed, but remains an unsolved problem when the only relaxation processes are those that arise from intermolecular dipolar interactions.

I. INTRODUCTION

It is well known that, at least from a theoretical point of view, a number of physical and chemical properties of two-dimensional (2*D*) systems are expected to be remarkably different from those of three-dimensional (3*D*) systems. Such properties include chemical reaction rates,[1] lateral diffusion,[2] the nature and order of phase transitions,[3] and various correlation functions,[4,5] especially those involved in the calculation of magnetic resonance line shapes. In evaluating such theoretical work the question is often raised as to whether or not a particular physical system is truly two dimensional. Certain problems involving the components of biological membranes are either strictly 2*D*, or sufficiently close to 2*D* that 2*D* theory must be used. This is the case for the theory of magnetic resonance line shapes, discussed here and earlier.[8] This problem is particularly troublesome since, as is well known, the correlation time for secular dipolar interactions is infinite for an infinite 2*D* membrane, even though the system is in every respect a 2*D* fluid where there is rapid molecular motion.[6] The purpose of the present paper is to provide a mathematical and physical understanding of this seemingly paradoxical result, by treating the problem for finite 2*D* systems, thereby laying the foundation for further work on the infinite 2*D* system.

We consider the case where the modulation of the secular dipole-dipole interaction, by the 2*D* Brownian diffusion, is the dominant mechanism for the relaxation. This can be useful for dilute gases[4] and liquids[5,7–11] and in some appropriate ranges of temperature and viscosity for biological membranes.[6,12–15] In the first part of the following section we give a general expression for the dipolar correlation function in a finite 2*D* spin system. This latter is expressed as a difference of a pairwise autocorrelation and cross-correlation terms which are significant for finite systems and ensure the decay to zero of the dipolar correlation function at infinite time. This is an extension to finite 2*D* system of a previous work on lattice correlation functions[4] calculated according to the well known Kubo's method.[8] In the second part we calculate this expression, using the Green's function method[16(a)] successively for infinite and finite planar surfaces. For the infinite surface this correlation function does not decay fast enough to define a correlation time. For a finite surface, one obtains an expression which is a function of the diffusion constant D, the distance of the closest approach between two spins δ, and the size of the system. This leads to a finite value of the correlation time. In the final part, we consider the motional narrowing effect in a finite planar spin system such as a spin-labeled phospholipid monolayer membrane. The narrowing condition[8] for each value of the spin concentration C and the diffusion constant D defines a maximum area of the spin system for which motional narrowing occurs. A range for the values of this size is given for electrons and protons.

II. THEORY

A. Dipolar correlation function in a finite two-dimensional spin system

We consider a system of $2N$ ($\gg 1$) electronic or nuclear spins with $S = 1/2$, belonging to the same species which diffuse on a finite 2*D* surface of area A in the presence of a strong constant magnetic field of intensity B_0. We consider only the relaxation due to the modulation of the secular dipole–dipole interaction by translational diffusion. Using a statistical approach, the persistence of the fluctuations of the local dipolar fields acting on an arbitrary test spin j due to all other spins $i (\neq j)$,[17] can be represented by the dipolar correlation function

$$G_j(\tau) \equiv G(\tau) = \left\langle \sum_{i=1}^{2N} b_{ij}(0) \sum_{i=1}^{2N} b_{ij}(\tau) \right\rangle . \quad (1)$$

Here

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$$b_{ij}(0)=\frac{3}{4}\frac{g^2\mu^2}{\hbar}(1-3\cos^2\theta_{ij})r_{ij}^{-3}n_i\ , \tag{2}$$

is the secular interaction between two spins,[10(b)] and $b_{ij}(\tau)$ the same quantity at a later time τ, and $n_i=\pm 1$ gives the orientations of the spin i assuming an orientation + for the test spin j. The notation $\langle\rangle$ corresponds to the ensemble averages over all the positions θ_{ij}, r_{ij}, and orientations n_i at times 0 and τ, respectively. Here θ_{ij} is the angle between the radius vector $\mathbf{r}_{ij}$ from i to j and direction of the field B_0.

It is possible to simplify Eq. (1) as follows: The separation of the contributions from the i's belonging to the up and down spins leads to the following sum of autocorrelation $G^{ac}(\tau)$ and cross-correlation $G^{cc}(\tau)$ functions

$$G(\tau)=G^{ac}(\tau)+G^{cc}(\tau)\ , \tag{3}$$

where

$$G^{ac}(\tau)=\sum_{i=1}^{2N}\langle b_{ij}(0)b_{ij}(\tau)\rangle\ , \tag{4}$$

$$G^{cc}(\tau)=\sum_{i\neq k=1}^{2N}{}'\langle b_{ij}(0)b_{kj}(\tau)\rangle\ . \tag{5}$$

Primes on summations indicate that terms for which $i=k$ are omitted. At high temperatures (~ 300 K) when the number of plus spins is very nearly equal to the number of minus spins,

$$G(\tau)=2N[\langle b_{ij}(0)b_{ij}(\tau)\rangle-\langle b_{ij}(0)b_{kj}(\tau)\rangle]\ . \tag{6}$$

In this latter equation the ensemble averages can be replaced by their usual expressions [(7) and (8)] in terms of the conditional probability $P(\mathbf{r}_i,\mathbf{r}_j,\tau\,|\,\mathbf{r}_{i_0},\mathbf{r}_{j_0},0)$ for the particle i to be at time τ at position $\mathbf{r}_i$ within the surface $d\mathbf{r}_i^2$ at a distance $\mathbf{r}_{ij}$ from a second particle j at $\mathbf{r}_j$ contained within $d\mathbf{r}_j^2$, when these two particles were at time $\tau=0$ at $\mathbf{r}_{i_0}$ and $\mathbf{r}_{j_0}$, respectively. This gives

$$\langle b_{ij}(0)b_{ij}(\tau)\rangle=\int d\mathbf{r}_{i_0}^2 p(\mathbf{r}_{i_0})\int d\mathbf{r}_{j_0}^2 p(\mathbf{r}_{j_0})b_{i_0j_0}\times\int d\mathbf{r}_i^2\int d\mathbf{r}_j^2 P(\mathbf{r}_i,\mathbf{r}_j,\tau\,|\,\mathbf{r}_{i_0},\mathbf{r}_{j_0},0)b_{ij}\ , \tag{7}$$

$$\langle b_{ij}(0)b_{kj}(\tau)\rangle=\int d\mathbf{r}_{i_0}^2 p(\mathbf{r}_{i_0})\int d\mathbf{r}_{j_0}^2 p(\mathbf{r}_{j_0})b_{i_0j_0}\times\int d\mathbf{r}_k^2 p(\mathbf{r}_k)\int d\mathbf{r}_j^2 p(\mathbf{r}_j)b_{kj}\equiv(\bar{b})^2\ , \tag{8}$$

where $p(\mathbf{r}_{i_0})=p(\mathbf{r}_{j_0})\equiv A^{-1}$ are the initial uniform distributions for i and j, and $\bar{b}$ is the average magnitude of the field between two particles randomly distributed in the area. By substituting Eqs. (7) and (8) into Eq. (6), we obtain the following general expression of the dipolar correlation function for a spin system diffusing on a finite $2D$ surface of area A:

$$G(\tau)=\left(\frac{2N}{A^2}\right)\left[\int d\mathbf{r}_{i_0}^2\int d\mathbf{r}_{j_0}^2\, b_{i_0j_0}\int d\mathbf{r}_i^2\int d\mathbf{r}_j^2\times P(\mathbf{r}_i,\mathbf{r}_j,\tau\,|\,\mathbf{r}_{i_0},\mathbf{r}_{j_0},0)b_{ij}-A^{-2}\left(\int d\mathbf{r}_{i_0}^2\int d\mathbf{r}_{j_0}^2\, b_{i_0j_0}\right)^2\right]\ . \tag{9}$$

As seen in Eq. (9), the decay of $G(\tau)$ depends on the form of the function P which is obtained by solving the diffusion equation. That solution depends on the size and geometry of the $2D$ surface. Concrete examples are presented in the next section for planar surfaces of different areas.

B. Dipolar translational correlation time in a planar spin system

For simplicity, let the high constant magnetic field B_0 be perpendicular to the $2D$ plane. This eliminates the explicit $\cos\theta_{ij}$ dependence in Eqs. (2)–(9). Two cases will be successively considered, infinite A and the finite A cases. In each case the normalized dipolar correlation function will be calculated from Eq. (9) and the average secular dipolar translational correlation time will be deduced.

1. Infinite planar area

For an infinite planar area ($A\to\infty$), the pairwise expression given in Eq. (9) can be greatly simplified. The cross-correlation term does not contribute here, and it is legitimate to consider one of the particles fixed at the origin and allow the other to diffuse radially with a double diffusion coefficient.[10(a),11] Using a delta function for the unit instantaneous material source released at time $\tau=0$ at the radius $r=r_0$,[16(b)] we can obtain the Green's function for an infinite system $P^{\mathrm{l.t.}}\sim(8\pi D\tau)^{-1}$ at long time (l.t.). Substituting the function $P^{\mathrm{l.t.}}$ in Eq. (9), one finds after some algebraic manipulations the normalized dipolar correlation function at long time

$$G_{N\,\mathrm{inf}}^{\mathrm{l.t.}}(\tau)=G_{\mathrm{inf}}^{\mathrm{l.t.}}(\tau)/G_{\mathrm{inf}}^{\mathrm{l.t.}}(0)\sim\delta^2/(D\tau)\ , \tag{10}$$

where δ is the distance of closest approach of pairs of spins. We see in Eq. (10) that for an infinite $2D$ surface $G_{N\,\mathrm{inf}}^{\mathrm{l.t.}}(\tau)$ does not decay fast enough, as shown previously,[4,5] to obtain a finite correlation time $\bar{\tau}_c$ [or zero-frequency spectral density $J(0)$] because of the logarithmic divergence of $J(\omega)$ as $\omega\to 0$:

$$\bar{\tau}_c\sim\int_0^\infty G_{N\,\mathrm{inf}}^{\mathrm{l.t.}}(\tau)dc=J(0)=\infty\ , \tag{11}$$

where $G_{N\,\mathrm{inf}}^{\mathrm{l.t.}}(\tau)$ is replaced in Eq. (11) by its expression given in Eq. (10). In that case, it is not possible to • apply the rapid motion narrowing theory of Kubo to obtain the line shape.

2. Finite planar area

For a finite planar surface of area A, the relative diffusion assumption used above cannot be applied. However, because the two random variables $\mathbf{r}_i$ and $\mathbf{r}_j$ are independent it is possible to consider the Green's function $P(\mathbf{r}_i,\mathbf{r}_j,\tau\,|\,\mathbf{r}_{i_0},\mathbf{r}_{j_0},0)$ present in Eq. (9) as a product of two Green's functions $P_i(\mathbf{r}_i,\tau\,|\,\mathbf{r}_{i_0},0)$ associated with each particle i ($i=1$ or 2). These latter functions can easily be found when one considers, as $2D$ finite planar area, a square of side a ($0\leq x,y\leq a$). If one assumes a unit instantaneous material line (parallel to the z axis) passing through the point x_{i_0}, y_{i_0} ($i=1$ or 2) at time $\tau=0$, and no diffusive flow out of the square, it has been shown[16(a)] that

$$P_i(x_i, y_i, \tau | x_{i_0}, y_{i_0}, 0) = a^{-2}\left[1 + 2\sum_{n=1}^{\infty} \exp(-n^2\pi^2 D\tau/a^2) C_n^a(x_i, x_{i_0})\right] \times \left[1 + 2\sum_{n=1}^{\infty} \exp(-n^2\pi^2 D\tau/a^2) C_n^a(y_i, y_{i_0})\right], \quad i = 1 \text{ or } 2, \tag{12}$$

using the notation

$$C_n^a(x_i \text{ or } y_i,\ x_{i_0} \text{ or } y_{i_0}) = \cos\left[n\frac{\pi}{a}(x_i \text{ or } y_i)\right] \cos\left[n\frac{\pi}{a}(x_{i_0} \text{ or } y_{i_0})\right]. \tag{13}$$

The pairwise Green's function $P(\mathbf{r}_1, \mathbf{r}_2, \tau | \mathbf{r}_{1_0}, \mathbf{r}_{2_0}, 0)$ is then obtained as the product $P_1 \times P_2$, where P_1 and P_2 are given in Eq. (12). This assumes that volume exclusion is not significant in the correlation of the interparticle distance. After a simple calculation one has

$$P(x_1, y_1, x_2, y_2, \tau | x_{1_0}, y_{1_0}, x_{2_0}, y_{2_0}, 0) = a^{-4}\Bigg\{1 + 2\sum_{n=1}^{\infty} \exp(-n^2\tau/2\tau_1) \sum_{i=1,2} C_{n+n}^a(i, i_0) + 4\sum_{n,m=1}^{\infty}\sum^{\infty} \exp[-(n^2+m^2)\tau/2\tau_1] \times\left[\sum_{i=1,2} C_{n\times m}^a(i, i_0) + C_{n+n}^a(1, 1_0) C_{m+m}^a(2, 2_0)\right] + 8\sum_{n,m,p=1}^{\infty}\sum^{\infty}\sum^{\infty} \exp[-(n^2+m^2+p^2)\tau/2\tau_1] \times \sum_{i\neq j=1,2} C_{n\times m}^a(i, i_0) C_{p+p}^a(j, j_0) + 16\sum_{n,m,p,q=1}^{\infty}\sum^{\infty}\sum^{\infty}\sum^{\infty} \exp[-(n^2+m^2+p^2+q^2)\tau/2\tau_1] C_{n\times m}(1, 1_0) C_{p\times q}(2, 2_0)\Bigg\}, \tag{14}$$

with the notations

$$\tau_1 = a^2/2\pi^2 D, \tag{15}$$

$$C_{n+n}^a(i, i_0) = C_n^a(x_i, x_{i_0}) + C_n^a(y_i, y_{i_0}), \tag{16}$$

$$C_{n\times m}^a(i, i_0) = C_n^a(x_i, x_{i_0}) \times C_m^a(y_i, y_{i_0}), \quad i = 1 \text{ or } 2. \tag{17}$$

The different terms in the series present in Eq. (14) can be regarded as coming from the superposition of the normal modes of diffusive relaxation in a square, starting at time $\tau = 0$ with two unit instantaneous material lines (one for each particle), respectively at (x_{1_0}, y_{1_0}) and (x_{2_0}, y_{2_0}) and represented by delta functions (Appendix A 2). These series converge rapidly due to the time-decaying exponentials. The exponents of those exponentials are expressed in terms of the longest correlation time τ_1 defined in Eq. (15). We have shown in Appendix A how each of these five series of terms contributes to the dipolar correlation function and obtained the normalized dipolar correlation function $G_N(\tau)$ for a finite plane area as

$$G_N(\tau) = \sum_{k=1}^{5} G_k(\tau)/G(0), \tag{18}$$

where the expressions of the five $G_k(\tau)$ and $G(0)$ are given in Eqs. (A1), (A4) [(A8), and (A14)], (A18) [(A22), and (A26)], respectively. The $G_k(\tau)$'s are expressed as sums of individual mode contributions. Each of these contributions is a product of a time-decaying exponential and an amplitude factor which represents a spatial oscillation. The decay constant of each mode τ_n varies approximately as τ_1/n^2. The spatial frequency of the oscillations depends on the value of the range of dipolar interaction $l\delta$ ($l \geq 1$) (δ being the distance of closest approach between two spins), the size of the system a, and the value of the mode n, through the product $n\pi l\delta/a$ for the condition: $\delta < l\delta \ll a$ (Appendix A). So, for a given value of the ratio $l\delta/a \ll 1$, the high spatial frequency terms ($n \gg 1$) decay faster than the low frequency ones ($n \sim 1$).

In order to have a more useful form for the line shape analysis it is possible to simplify greatly the expression of $G_N(\tau)$. For instance, according to the assumption $l\delta/a \ll 1$, most of the terms of Eq. (18) have a very small amplitude and we neglect these terms of order $l\delta/a$ which give very small contributions to the line shape. Computer calculations of the amplitudes of the different $G_k(\tau)$ have shown that the following convergent expression represents, at time $\tau = 0$, 99% of the total power $G_N(0)$.

$$G_N(\tau) \sim \sum_{n=1}^{\infty} b_n \exp(-n^2\tau/\tau_1) + \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} b_{nm} \exp[-(n^2+m^2)\tau/\tau_1] + \cdots, \tag{19}$$

where

$$b_n = 8(\delta/a)^2 Z_n^2 B_n^2, \tag{20a}$$

$$b_{nm} = 4(\delta/a)^2 Z_n^2 Z_m^2 B_{nm}^2. \tag{20b}$$

Here Z_n, B_n, B_{nm} are functions of δ, a, and n, which are defined in Eqs. (A16), (A17), and (A23), respectively.

In order to estimate the rate of decay of $G_N(\tau)$ we can use an "average" translational correlation time $\overline{\tau}_c$ defined by

$$\overline{\tau}_c = \int_0^{\infty} G_N(\tau)\, d\tau = \frac{4}{\pi^2}\left(\frac{\delta^2}{2D}\right)\left[2\sum_{n=1}^{\infty} Z_n^2 B_n^2/n^2 + \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} Z_n^2 Z_m^2 B_{nm}^2/(n^2+m^2)\right], \tag{21}$$

where we have replaced $G_N(\tau)$ by its expression given in Eq. (19). We have displayed in Fig. 1 the variations of $\overline{\tau}_c/(\delta^2/2D)$ with the size of the system expressed by the ratio a/δ. It is interesting to note that $\delta^2/2D$ corre-

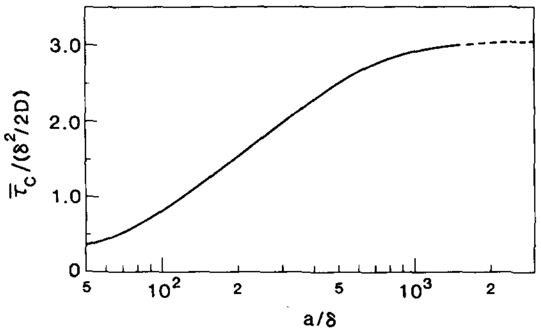

FIG. 1. Semilogarithmic plot of $\overline{\tau}_c/(\delta^2/2D)$ vs a/δ. The solid line corresponds to computer calculations of Eq. (21). The dotted line shows the weak logarithmic increase of $\overline{\tau}_c$ when $a \gg \delta$ (Eq. 22).

sponds to the constant limit value of the translational correlation time obtained for an infinite three-dimensional system.[10(a)] The increase of $\overline{\tau}_c$ with the size of the system comes from the convergent expression in brackets in Eq. (21) which has been calculated using a computer. In the limit of an infinite $2D$ system, one has $a \to \infty$ and it is easy to show that $Z_n \to 1$ and B_n and B_{nm} tends to $1-\sigma(l^{-1})$. With the relations[18,19]

$$\sum_{n=1}^{\infty} 1/n^2 = \pi^2/6 \ ,$$

$$\sum_{n=1}^{\infty}\sum_{m=1}^{\infty} 1/(n^2+m^2) = \frac{\pi}{2}\sum_{n=1}^{\infty}\frac{\coth n\pi}{n} - \frac{\pi^2}{12} \ ,$$

one has the following limiting expression for $\overline{\tau}_c$:

$$\overline{\tau}_c = [1-\sigma(l^{-1})]^2 \frac{\delta^2}{2D}\left[1 + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{\coth n\pi}{n}\right] \ , \qquad (22)$$

where the sum on n diverges logarithmically when $n \to \infty$. So we obtain the same weak logarithm divergence as that shown in Eq. (11).

C. Motional narrowing in a finite planar spin system

It is well known that dipolar interactions, in nuclear or paramagnetic spin systems, are modulated by the motions of the spins. This modulation, when it is sufficiently rapid, can average out the dipolar interactions and consequently leads to an important narrowing of the resonance lines. The theory of this motional narrowing has been previously described for an infinite $3D$ spin system.[8] Its application to an infinite $2D$ spin system[4] is difficult due to the result obtained in Eq. (11). However, owing to the finite value of $\overline{\tau}_c$ obtained in Eq. (21), it becomes possible now to apply this theory to the finite $2D$ case.

According to this theory and introducing the line width $\Delta\omega_G$ in the rigid lattice limit, the line becomes narrowed if the condition, $\Delta\omega_G\overline{\tau}_c \ll 1$, is satisfied. In this case of fast modulation the line becomes a Lorentzian with a half-height half-width $\Delta\omega_L = \Delta\omega_G^2\overline{\tau}_c$.[8] Using a statistical theory[10(b),20] for the rigid lattice limit, we have calculated in Appendix B the linewidth $\Delta\omega_G(R, N_A \equiv 2N/A)$ for a finite $2D$ planar spin system as described above, and found

$$\Delta\omega_G(R,N_A) = 2.528\left(\frac{g^2\mu^2}{\hbar}\right) \times \left[\frac{1+0.415N_A^{-2}R^{-4}+\sigma(N_A^{-5}R_A^{-10})}{1+5.087N_A^{-2}R^{-4}+\sigma(N_A^{-5}R_A^{-10})}\right]^{1/2} N_A^{3/2} \ , \qquad (23)$$

where R is the radius of the system. If we consider a constant surface density N_A through the sample and assume that the spins are distributed randomly over the N_0 sites available in this sample with the concentration $C = 2N/N_0$, we have $N_A = C/A_{1_s}$, where A_{1_s} represents the area of a single site. Knowing C and A_{1_s}, it becomes possible to get an estimate of the radius R_{90} of the system surrounding the test spin j for which one has 90% of the maximum value $\Delta\omega_G(\infty, N_A)$ obtained from the limit of Eq. (23) for $R \to \infty$. This has been considered below in a particular case.

Consider as a $2D$ planar spin system the case of a spin-labeled phospholipid membrane where the area per lipid molecule A_{1_s} is of the order of 64 Å^2 and the distance of the closest possible approach δ is around 8 Å. In the case where there is no diffusion the line is Gaussian with a width $\Delta\omega_G$ corresponding to the rigid lattice limit given in Eq. (23) (Appendix B). In this case, we have displayed in Fig. 2, the variations of the ratio $\Delta\omega_G(R,C)/\Delta\omega_G(\infty,C)$ with R for different concentrations C. We see on these curves that R_{90} decreases when C increases taking the following values: 307, 168.2, 97, and 53.2 Å when C is 0.003, 0.01, 0.03, and 0.1, respectively. In the case of rapid modulation ($\overline{\tau}_c \ll \Delta\omega_G^{-1}$) the diffusion is sufficiently rapid to obtain a motional narrowing of the line. The line becomes Lorentzian with a width $\Delta\omega_L = \Delta\omega_G^2\overline{\tau}_c$ where $\Delta\omega_G$ and $\overline{\tau}_c$ are given in Eqs. (21) and (23), respectively. In this case, we have displayed in Fig. 3 the variations of the narrowing condition, $\Delta\omega_G(R_{90},C)\overline{\tau}_c(D,a/\delta) = \Delta\omega_L/\Delta\omega_G \ll 1$, with the size of the system a/δ for different concentrations C. Here D has been chosen to be the average value found for these systems $\sim 10^{-8}$ cm^2/s and we consider the spin electronic value $g\mu_0$ in Eq. (23). We see on these curves that the narrowing condition is better satisfied for low concentration ($C = 0.003$) than for high concentration ($C = 0.03$). This is due to the concentration variation of the static linewidth $\Delta\omega_G(R_{90},C)$ which is proportional to $C^{3/2}$. In other words the percentage of narrowing $1 - \Delta\omega_L/\Delta\omega_G$ for some values of C, D, and a is more important when the concentration decreases, a result previously observed in these systems.[13(b)] In the pres-

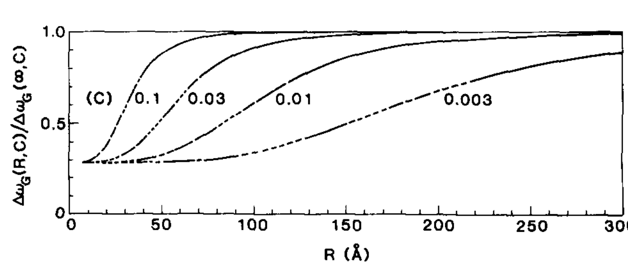

FIG. 2. Plot of $\Delta\omega_G(R,C)/\Delta\omega_G(\infty,C)$ vs R in Å for different values of the the spin concentration C (rigid lattice condition). The solid lines correspond to the region of R (for fixed values of C) where the limited expansion given in Eq. (B8) occurs.

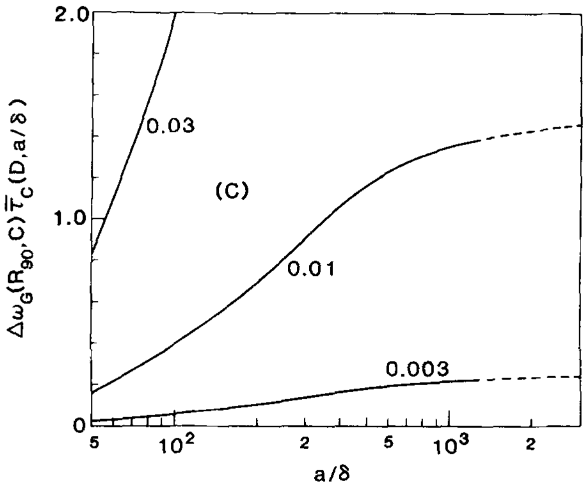

FIG. 3. Semilogarithmic plot of the product $\Delta\omega_G(R_{90}, C)\bar{\tau}_c(D, a/\delta)$ vs a/δ for different values of the spin concentration C and with $D = 10^{-8}$ cm^2/s, $\delta = 8$ Å and the value $g\mu_0$ in Eq. (23) for electronic spins (ESR case).

ence of inhomogeneously broadened lines[21] a fast deconvolution procedure may be needed to extract $\Delta\omega_L$ from the observed linewidth.[22]

As the maximum value of $\Delta\omega_L$ is $\Delta\omega_G$, it is also possible to define for each value of C and D a maximum size of the system $a_{\max}$ from the solution of the narrowing condition in the limit case where

$$\Delta\omega_G(R_{90}, C)\bar{\tau}_c(D, a_{\max}/\delta) = \frac{\Delta\omega_L}{\Delta\omega_G} = 1 \ . \quad (24)$$

For the ESR case the range of the values found for $a_{\max}$ stands between 10^2 and $\sim 10^3\delta$ or much more depending on the value of C and D. For the proton NMR case, the values found for $a_{\max}$ are much higher (macroscopic values) due to the low value of $\Delta\omega_G(R_{90}, C)$ found for the protons which is about 10^6 smaller than that of the electrons ($\bar{\tau}_c$ being naturally the same in the two cases). So, for each value of C, D, and δ, Eq. (24) gives a physical reason to take a finite size of the spin system under which the condition of fast modulation is verified and the motional narrowing occurs.

III. CONCLUSION

We have used a statistical method to calculate the correlation function for the secular part of the dipolar relaxation processes in a finite two-dimensional spin system. This led to a general expression of the dipolar correlation function $G(\tau)$ represented as a difference of a pairwise autocorrelation and cross-correlation terms, the latter being significant for finite systems. We have shown that $G(\tau)$ for a finite $2D$ plane surface decays more rapidly than $G(\tau)$ for an infinite plane surface. The translational correlation time obtained for these surfaces can be useful in the measurements of the lateral diffusion constant D of spin labels or intrinsic probes embedded in a planar membrane. For sufficiently small, finite $2D$ systems one obtains narrowing conditions for each value of the spin concentration and diffusion coefficient D. The method used in this work can be useful for those who are interested in how magnetic resonance might be employed to study motion in restricted environments. The calculation of resonance line shapes for infinite $2D$ systems where there is rapid motion is a problem that remains to be solved, and this problem is left for subsequent work. It has been pointed out earlier that if there is some (rapid) T_1 relaxation process, not explicitly dependent on $2D$ lateral diffusion, then the relaxation process provides a natural cutoff of the long-time decay of $G(\tau)$ for the infinite system. It will be necessary to make a careful analysis of the effects of intermolecular dipolar interactions on T_1 relaxation for the infinite system to determine if this relaxation due to translational diffusion can provide a truncation of the otherwise long-time decay of $G(\tau)$ for the infinite two-dimensional system.

APPENDIX A: DIPOLAR CORRELATION FUNCTION FOR A FINITE PLANAR SURFACE

In this Appendix we calculate successively the five terms $G_k(\tau)$ $k \in \{1, \ldots, 5\}$ obtained when one substitutes the five series of terms of Eq. (14) with Eq. (13), and Eqs. (15)–(17) into Eq. (9).

1. Calculation of the $G_k(\tau)$

a. $G_1(\tau)$

Substitution of the first term $a^{-4} = A^{-2}$ of Eq. (14) into Eq. (9) leads to an expression which is equal to the cross-correlation term $G^{cc}(\tau)$, so one has

$$G_1(\tau) = G^{cc}(\tau) - G^{cc}(\tau) = 0 \ . \quad (A1)$$

b. $G_2(\tau)$

Substituting the second series of terms of Eq. (14) into Eq. (9) when using Eq. (2) with $\theta_{12} = \pi/2$, Eqs. (13) and (15)–(17) and with the different symmetries, one has

$$G_2(\tau) = 8\alpha^2 N_A A^{-3} \sum_{1n} \exp(-n^2\tau/2\tau_1) \times \left[\int_{R_l}^{a-R_l} dx_1 \cos n\pi\frac{x_1}{a} \int_{R_l}^{a-R_l} dy_1 H_{21}\right]^2 . \quad (A2)$$

Here $1n$ is a notation for $n \in \{1, \ldots, \infty\}$ (n integer), $\alpha = 3g^2\mu^2/4\hbar$, $A = (a - 2R_e)^2$ is the nonhatched area in Fig. 4, $N_A = 2N/A$ and H_{21} is proportional to the expected field at particle 1 due to particle 2 limited to the radial domain $\delta \le r \le R_l$ centered about each position of 1 (Fig. 4).

$$H_{21} = \int_{R_l}^{a-R_l} dx_2 \int_{R_l}^{a-R_l} dy_2\, r^{-3} \sim \int_0^{2\pi} d\theta \int_\delta^{R_l} dr\, r^{-2} = \delta^{-1}[1 - \sigma(l^{-1})] , \quad (A3)$$

where $r \equiv [(x_2 - x_1)^2 + (y_2 - y_1)^2]^{+1/2}$ and $R_l \equiv l\delta$ ($l \ge 1$) a multiple of δ. The contribution of the hatched region has been removed in order to have a finite result for Eq. (A2) and the possibility to have $\theta \in [0, 2\pi]$ in Eq. (A3). This limitation is valid providing $l\delta/a \ll 1$. Substitution of Eq. (A3) into Eq. (A2) leads to

$$G_2(\tau) = 32\pi[1 - \sigma(l^{-1})]^2 \sum_{2n} \exp(-n^2\tau/2\tau_1) X_n^2 , \quad (A4)$$

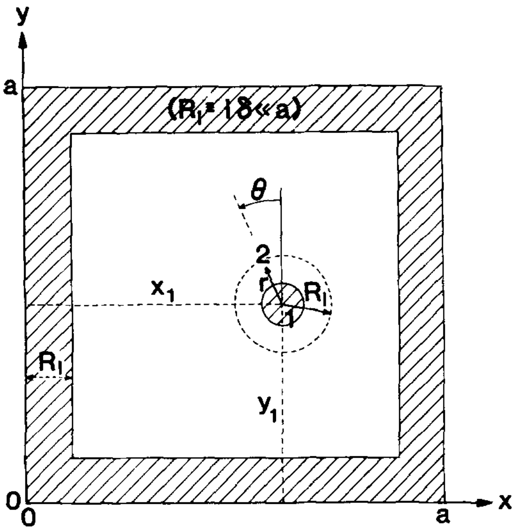

FIG. 4. The square surface of side a. The particles 1 and 2 are spatially distributed according to the various terms of Eq. (14). For each position of these particles, the integrations are limited to the nonhatched region. The field B_0 is perpendicular to the plane of the figure.

introducing the notations

$$\mathfrak{N} = 2\pi\alpha^2 N_A (a\delta)^{-2} , \tag{A5}$$

$$X_n = \sin(n\pi l\delta/a)/(n\pi) ,$$

$$2n \text{ stands for } n \in \{2, \ldots, \infty\} \text{ with } n \text{ even} . \tag{A6}$$

c. $G_3(\tau)$

Substituting the third series of terms of Eq. (14) into Eq. (9), one can separate $G_3(\tau)$ into two parts

$$G_3(\tau) = G_{31}(\tau) + G_{32}(\tau) . \tag{A7}$$

The first one, $G_{31}(\tau)$, comes from the $C^a_{n\times m}(i, i_0)$ defined in Eq. (17) and leads to the following result:

$$G_{31}(\tau) = 128\mathfrak{N}[1 - \sigma(l^{-1})]^2 \times \sum_{2n}\sum_{2m} \exp[-(n^2+m^2)\tau/2\tau_1] X_n^2 X_m^2 , \tag{A8}$$

which can be obtained in following the same procedure as that for $G_2(\tau)$.

The second one $G_{32}(\tau)$ comes from the $C^a_{n+n}(1, 1_0) \times C^a_{m+m}(2, 2_0)$ defined in Eq. (16) and is given by

$$G_{32}(\tau) = 8\alpha^2 N_A A^{-3} \sum_{1n}\sum_{1m} \exp[-(n^2+m^2)\tau/2\tau_1][I^2_{nm} + J^2_{nm}] , \tag{A9}$$

taking account of the different symmetries. In Eq. (A9) one has

$$I_{nm} = \int_{R_l}^{a-R_l} dx_1 \cos\left(n\pi\frac{x_1}{a}\right) \int_{R_l}^{a-R_l} dy_1 H_m(x_1, y_1) , \tag{A10}$$

$$J_{nm} = \int_{R_l}^{a-R_l} dx_1 \cos\left(n\pi\frac{x_1}{a}\right) \int_{R_l}^{a-R_l} dy_1 F_m(x_1, y_1) , \tag{A11}$$

introducing here H_m and F_m which are proportional to the expected fields at particle 1

$$H_m(x_1, y_1) = \int_{R_l}^{a-R_l} dx_2 \cos\left(m\pi\frac{x_2}{a}\right) \int_{R_l}^{a-R_l} dy_2\, r^{-3}$$

$$\sim \int_0^{2\pi} d\theta \int_\delta^{R_l} dr\, r^{-2} \cos\left[m\frac{\pi}{a}(x_1 - r\sin\theta)\right] = 2\pi\cos\left(m\frac{\pi}{a}x_1\right) \int_\delta^{R_l} dr\, r^{-2} J_0\left(m\frac{\pi}{a}r\right) , \tag{A12}$$

$$F_m(x_1, y_1) = 2\pi\cos\left(m\frac{\pi}{a}y_1\right) \int_\delta^{R_l} dr\, r^{-2} J_0\left(m\frac{\pi}{a}r\right) , \tag{A13}$$

using the integral representation of the Bessel function J of zero order in Eqs. (A12) and (A13). The substitution of Eqs. (A12) and (A13), respectively, into Eqs. (A10) and (A11), and finally into Eq. (A9) leads, after some algebraic manipulations, to

$$G_{32}(\tau) = \mathfrak{N}\left\{8\sum_{3nm}\sum \exp[-(n^2+m^2)\tau/2\tau_1] Y^2_{nm} B^2_m + 2\sum_{1n} \exp(-n^2\tau/\tau_1) Z^2_n B^2_n + 128\sum_{2n}\sum_{2m} \exp[-(n^2+m^2)\tau/2\tau_1] X^2_n X^2_m B^2_m\right\} , \tag{A14}$$

with the notations

$$Y_{nm} = \left[\frac{\sin(m-n)\pi l\delta/a}{(m-n)\pi} + \frac{\sin(m+n)\pi l\delta/a}{(m+n)\pi}\right] , \tag{A15a}$$

$$\text{where } 3nm \text{ stands for } n, m \in \{1, \ldots, \infty\} \text{ with } n^2 \neq m^2 \text{ and } n \pm m \text{ even} , \tag{A15b}$$

$$Z_n = \left[1 - 2l\delta/a - \frac{1}{n\pi}\sin(2n\pi l\delta/a)\right] , \tag{A16}$$

$$B_n = \delta \int_\delta^{l\delta} dr\, r^{-2} J_0\left(n\frac{\pi}{a}r\right) . \tag{A17}$$

It should be noted that the functions X_n, Y_{nm}, Z_n, and B_n defined in Eqs. (A6) and (A15)–(A17) are functions of the range of dipolar interactions $l\delta$, the size of the system a and the value of the mode n. The integral in Eq. (A17) cannot be expressed simply and has been calculated numerically when replacing the Bessel function J_0 by its power series.

d. $G_4(\tau)$

Substituting the fourth series of terms of Eq. (14) into Eq. (9) one can obtain with the same procedure used for $G_{32}(\tau)$,

$$G_4(\tau)=\mathfrak{N}\left\{128\sum_{3np}\sum\sum_{2m}\exp[-(n^2+m^2+p^2)\tau/2\tau_1]Y^2_{np}X^2_m B^2_p+32\sum_{1n}\sum_{2m}\exp[-(2n^2+m^2)\tau/2\tau_1]Z^2_n X^2_m B^2_n\right\} . \quad (A18)$$

e. $G_5(\tau)$

Substituting the fifth series of terms of Eq. (14) into Eq. (9) leads to

$$G_5(\tau)=16\alpha^2 N_A A^{-3}\sum_{1n}\sum_{1m}\sum_{1p}\sum_{1q}\exp[-(n^2+m^2+p^2+q^2)\tau/2\tau_1]I^2_{nmpq} , \quad (A19)$$

where

$$I_{nmpq}=\int_{R_l}^{a-R_l}dx_1\cos\left(n\frac{\pi}{a}x_1\right)\int_{R_l}^{a-R_l}dy_1\cos\left(m\frac{\pi}{a}y_1\right)\int_{R_l}^{a-R_l}dx_2\cos\left(p\frac{\pi}{a}x_2\right)\int_{R_l}^{a-R_l}dy_2\cos\left(q\frac{\pi}{a}y_2\right) . \quad (A20)$$

This latter integral can be calculated using the associate series of Bessel functions

$$\cos(z\sin\theta)=J_0(z)+2\sum_{1k}J_{2k}(z)\cos 2k\theta \quad (A21)$$

and similar series for $\sin(z\sin\theta)$, $\cos(z\cos\theta)$, and $\sin(z\cos\theta)$.[18] After some algebraic calculations similar as those proceeded above, one finds

$$G_5(\tau)=\mathfrak{N}\left\{\sum_{1n}\sum_{1m}\exp[-(n^2+m^2)\tau/\tau_1]Z^2_n Z^2_m B^2_{nm}+8\sum_{1n}\sum_{3mp}\sum\sum\exp[-(2n^2+m^2+p^2)\tau/2\tau_1]Z^2_n Y^2_{mp} B^2_{np}\right.$$
$$\left.+16\sum_{3nm}\sum\sum_{3pq}\sum\exp[-(n^2+m^2+p^2+q^2)\tau/2\tau_1]Y^2_{nm}Y^2_{pq}B^2_{nq}\right\} , \quad (A22)$$

where

$$B_{nm}=\delta\int_\delta^{16}dr\,r^{-2}J_0\left(n\frac{\pi}{a}r\right)J_0\left(m\frac{\pi}{a}r\right) . \quad (A23)$$

This last integral cannot be expressed simply and has been calculated numerically replacing the Bessel functions by their power series.

2. Calculation of $G(0)$

In order to calculate the normalized dipolar correlation function $G_N(\tau)\equiv G(\tau)/G(0)$ we need to know $G(0)$. The expression presented in Eq. (14) is not very well adapted to the situation at short time. However, it is possible to transform Eq. (12) with application of Poisson's formula,[16(d)] and this gives

$$P_i(x_i,y_i,\tau\,|\,x_{i_0},y_{i_0},0)=(1/4\pi D\tau)\left[\sum_{n=-\infty}^{+\infty}\{\exp[-(x_i-x_{i_0}+2na)^2/4D\tau]+\exp[-(x_i+x_{i_0}+2na)^2/4D\tau]\}\right]$$
$$\times\left[\sum_{n=-\infty}^{+\infty}\{\exp[-(y_i-y_{i_0}+2na)^2/4D\tau]+\exp[-(y_i+y_{i_0}+2na)^2/4D\tau]\}\right] ,\quad i=1 \text{ or } 2 . \quad (A24)$$

If one assumes a unit instantaneous material line (parallel to the z axis) passing through the point x_{i_0}, y_{i_0} ($i=1$ or 2) at time $\tau=0$, one has

$$\lim P_i=\delta(x_i-x_{i_0})\delta(y_i-y_{i_0})$$

and consequently for the limiting value of Eq. (14) at time $\tau=0$, one has

$$P_0=\delta(x_1-x_{1_0})\delta(y_1-y_{1_0})\delta(x_2-x_{2_0})\delta(y_2-y_{2_0}) . \quad (A25)$$

Substituting this value of P_0 into Eq. (9) one easily finds

$$G(0)=\pi N_A\alpha^2/(2\delta^4) . \quad (A26)$$

The normalized dipolar correlation function is then defined by

$$G_N(\tau)\equiv G(\tau)/G(0)=\sum_{k=1}^{5}G_k(\tau)/G(0) . \quad (A27)$$

APPENDIX B: LINEWIDTH ANALYSIS FOR A FINITE 2D PLANAR SPIN SYSTEM IN THE RIGID LATTICE LIMIT

In this Appendix, we apply a well-known statistical theory of line broadening[10(b),20] to obtain the linewidth, in the rigid lattice limit, of an ensemble of $2N$ spins $S=1/2$ submitted to the same conditions as described in Sec. II A and II B and diluted in a $2D$ finite plane of area A. In this theory the intensity of absorption $I(\omega)d\omega$ is proportional to the area of the 2N dimensional phase space

$$I(\omega)d\omega = A^{-2N}\int_{E(\omega,d\omega)} d^2\mathbf{r}_1\cdots d^2\mathbf{r}_{2N}\ , \qquad \text{(B1)}$$

restricted to the region $E(\omega, d\omega)$ of the phase space where the following condition is satisfied:

$$\omega \le \omega(\mathbf{r}_1,\ldots,\mathbf{r}_{2N}) = \sum_{i=1}^{2N}\omega(\mathbf{r}_i) \le \omega + d\omega\ . \qquad \text{(B2)}$$

Here $\mathbf{r}_i$ is a vector indicating the relative position between one of the 2N spins i and the test spin j which is placed at the origin of the coordinates, and $\omega(\mathbf{r}_1,\ldots,\mathbf{r}_{2N})$ represents the departure from the mean Larmor frequency $\omega_0=\gamma B_0^z$, $\omega(\mathbf{r}_i)$ being one of the 2N spin dipolar contributions. The latter is given in Eq. (2) where we take $\theta_{ij}=\pi/2$ for simplification. Equation (B1) can be rewritten as an integral over the whole phase space

$$I(\omega)d\omega = d\omega A^{-2N}\int_{A^{2N}}\delta[\omega-\omega(\mathbf{r}_1,\ldots,\mathbf{r}_{2N})]d^2\mathbf{r}_1\cdots d^2\mathbf{r}_{2N}\ . \qquad \text{(B3)}$$

Taking an orientation (+) for the spin of j, using the integral definition of the delta function, one can modify Eq. (B3) after separation of the respective contributions from the up and down spins

$$I(\omega) = (2\pi)^{-1}\int_{-\infty}^{+\infty} dt\exp(i\omega t)\left[A^{-1}\int_A \exp(-ibtr^{-3})d^2r\right]^N \times\left[A^{-1}\int_A \exp(ibtr^{-3})\,d^2r\right]^N\ , \qquad \text{(B4)}$$

where we have used the radial coordinates r for the distance of the spins i from the origin at j with $A=\pi R^2$, R being the radius of the system, and with introduction of the notation

$$b=\tfrac{3}{4}g^2\mu^2/\hbar\ . \qquad \text{(B5)}$$

Following the same procedure as used in Ref. 10(b), Eq. (B4) becomes

$$I(\omega)=(2\pi)^{-1}\int_{-\infty}^{+\infty} dt\exp(i\omega t)\exp[-N_A J(R,b,t)]\ , \qquad \text{(B6)}$$

when $N_A=2N/A$ is the density of spins and

$$J(R,b,t)=2\pi\int_0^R[1-\cos(btr^{-3})]\,r\,dr \sim \pi(bt)^{2/3}S(bt/R^3,1/3)\ , \qquad \text{(B7)}$$

introducing here the Pearson's form of the incomplete gamma function S.[23] Owing to the relation $bt/R^4\ll 1$ one can replace S by its first order expansion, giving

$$J(R,b,t)\sim \tfrac{1}{2}\pi\,\Gamma(1/3)(bt)^{2/3}-\tfrac{3}{4}\pi\,(bt)^2/R^4+\sigma(R^{-10})\ . \qquad \text{(B8)}$$

Substitution of Eq. (B8) into Eq. (B6) gives

$$I(\omega)\sim\pi^{-1}\int_0^\infty \cos\omega t\exp\left[-\left(dt^{2/3}-\frac{c}{R^4}t^2\right)\right]dt\ , \qquad \text{(B9)}$$

with

$$c=\tfrac{3}{4}\pi b^2 N_A\ , \qquad \text{(B10a)}$$

$$d=\tfrac{1}{2}\pi\,\Gamma(1/3)b^{2/3}N_A\ . \qquad \text{(B10b)}$$

Owing to the values of the coefficients b, c, and d and the fact that $\omega^2/d^3\ll 1$, one can expand $\cos\omega t$ in Eq. (B9) in a power series and the integral is done term by term. Near $\omega\simeq 0$ (the important region for the line shape) $I(\omega)$ is approximated by a Gaussian with a width given by

$$\Delta\omega_G(R,N_A)=2.528\left(\frac{g^2\mu^2}{\hbar}\right)\times\left[\frac{1+0.415N_A^{-2}R^{-4}+\sigma(N_A^{-5}R_A^{-10})}{1+5.087N_A^{-2}R^{-4}+\sigma(N_A^{-5}R_A^{-10})}\right]^{1/2}N_A^{3/2}\ . \qquad \text{(B11)}$$

This Gaussian approximation is necessary because the moments of the super-Lorentzian $I(\omega)$ do not exist. For an infinite size of the system $\Delta\omega_G(\infty,N_A)$ is given by the limit of Eq. (B11) when $R\to\infty$

$$\Delta\omega_G(\infty,N_A)=2.528\,(g^2\mu^2/\hbar)N_A^{3/2}\ . \qquad \text{(B12)}$$

As expected, the 2D static linewidth is proportional to $N_A^{3/2}$, whereas the 3D static linewidth is proportional to N_A.[10(b),20]

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